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13. ABSTRACT (Maximum 200 words) The applied ends of the URI on advanced cryogenic propellants, namely the feasibility of preparing cryogenic materials with higher energy density than systems presently in use, have been met with two examples: solid hydrogens doped with atomic oxygen, and solid oxygen doped with atomic oxygen. Both of these systems have been demonstrated in the laboratory, and in the latter case, where doping number densities of order 1% have been achieved, a patent has been filed on the "Method for producing High Energy density Cryogenic Fuel". Additionally, methods of characterization, including quantitative calorimetry and spectroscopy, have been devised and implemented. The original proposal recognized the need for developing a fundamental scientific basis for such intended applications. There has been significant progress in this regard, developments that go beyond the immediate target of the URI. Practical methods for computation of energetics and dynamics in quantum hosts, and quantum many-body dynamics in extended systems, were developed and successfully applied. The rheology of solid hydrogens was studied, and characterized. Time resolved spectroscopic methods were devised and implemented to demonstrate that microscopic details inaccessible in frequency domain spectroscopy of condensed					
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Advance Cryogenic Propellants

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Fourth, FY '96 - '97, & Final Research Report

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Synopsis

The applied ends of the URI on advanced cryogenic propellants, namely the feasibility of preparing cryogenic materials with higher energy density than systems presently in use, have been met with two examples: solid hydrogens doped with atomic oxygen, and solid oxygen doped with atomic oxygen. Both of these systems have been demonstrated in the laboratory, and in the latter case, where doping number densities of order 1% have been achieved, a patent has been filed on the "*Method for producing High Energy Density Cryogenic Fuel*". Additionally, methods of characterization, including quantitative calorimetry and spectroscopy, have been devised and implemented. The original proposal recognized the need for developing a fundamental scientific basis for such intended applications. There has been significant progress in this regard, developments that go beyond the immediate target of the URI. Practical methods for computation of energetics and dynamics in quantum hosts, and quantum many-body dynamics in extended systems, were developed and successfully applied. The rheology of solid hydrogens was studied, and characterized. Time resolved spectroscopic methods were devised and implemented to demonstrate that microscopic details inaccessible in frequency domain spectroscopy of condensed media, could be unravelled with unprecedented detail. Approaches to soft landing of dopants for preparative physics of cryogenic propellants were investigated by characterizing pick-up by superfluid He clusters of a variety of dopants, and mass spectrometric methods for the characterization and analysis of such doped He clusters, were developed. Along the way, there have been detours and deviations from the initial plans, some, influenced by developments in programmatic considerations by the AF, and some motivated by the opportunities to make contributions of general intrinsic scientific value. Further, the URI has supported and developed a significant number of young scientists, students and postdocs, while exposing them to the High Energy Density Materials development mission of the AF.

I. ORIGINAL GOALS

The proposal for the URI identified the following applied science goals:

1. to create the fundamental data base needed to establish feasibility,
2. to devise, and optimize methods of preparation,
3. to prepare laboratory samples,
4. to devise and implement methods of characterization of both structure and dynamics in such samples,
5. to address issues of stabilization and scale-up,
6. to explore the rheology of multiphase slushes,
7. to collaborate with AF labs to conduct field tests.

Many of these goals have been met, with various levels of accomplishment. The original proposal also foresaw H doped solid hydrogens as the prototype to be characterized in some detail. However, this direction was abandoned, due to the change of direction in the AF labs, based on considerations of implementation. Instead, as a prototype, solid hydrogens and molecular oxygen doped with atomic oxygen were considered in some detail. A variety of other systems, such as doped solid He, superfluid He, superfluid He clusters, were considered as prototypes of non reactive quantum hosts, and as media for preparation and delivery of cryogenic propellants. We briefly address the extent of progress in the above identified goals, and follow it by more detailed highlights of the research accomplished under this program.

II. ACCOMPLISHED APPLIED GOALS

1. The Phillips Laboratory at AF Edwards Base has identified target cryogenic propellants of desirable specific impulse, mainly, solid hydrogen doped with a variety of low mass dopants. Based on pair potentials, and spin induced barriers to reaction, we have contributed to this list, and suggested that F, N, O doped solids should be feasible. The system of highest payoff, namely C doped H_2 , remains subject of some uncertainty. Our efforts at developing a discharge coupled C atom source for cryogenic depositions, were mainly unsuccessful, and therefore not conclusive. Both N doped and O doped H_2 has been demonstrated, and their stability with respect to reaction has been verified.

Beside the doping of solid H_2 with first row atomic impurities, the extent of diffusion, and diffusion induced recombination of impurities has been a major concern. In the case of O doped solid H_2 , we have experimentally demonstrated that the centers are less mobile than the host, and that the recombination onset corresponds to gross morphological changes associated with the softening and evaporation of the lattice. This is an important finding, that has also been verified theoretically: O doped solid H_2 is more stable than pure solid H_2 . Nevertheless, recombination temperatures remain below 9 K in D_2 , and 6 K in solid H_2 (these

constitute the highest temperatures reached prior to observation of $O + O$ recombination). We had also proposed that such samples may be stabilized by applied pressure. Indeed, we have demonstrated that when over-coated with Xe, samples of O doped H_2 could be heated to temperatures as high as 22 K, without inducing dimerization.

We believe, feasibility of the initial concept, at least the preparation of samples, their relative stability, and stabilization by applied pressure have been demonstrated.

2. Several methods of preparation of doped cryogenic solids: in situ photodissociation, soft landing of doped He clusters, deposition from DC discharge coupled atomic sources, and microwave and RF coupled discharges are examples that were devised and tested to different extent. Of these, the most successful development was the RF coupled oxygen atom source, which produced nearly pure atomic oxygen, and its affluent could be directly condensed to produce large number densities of O atoms trapped in solid oxygen. This source is rather delicate, but well characterized using a variety of diagnostics.

3. Laboratory samples of O doped solid H_2 and D_2 were prepared through in situ photolysis of molecular oxygen, and O doped solid oxygen was prepared by quench condensing the RF coupled O atom source.

4. Research carried under this grant has generated some of the most detailed spectroscopy of dopants in cryogenic solids, by developing both experimental and theoretical tools of analysis. The spectroscopy of O_2 doped solid hydrogens is among the best characterized. In this case, we know the structure of the local site (dominated by hcp) and even the orientation of the molecule relative to the lattice, further, in more recent demonstration experiments on NO doped solid H_2 , we have demonstrated that not only the dopant but also its nearest neighbors can be Spectroscopically tagged and identified through radiation induced spin flip of nearest neighbors. More generally, methods of ultrafast spectroscopy were developed, and demonstrated that in the case of solids they can be applied with unprecedented detail to the characterization of interactions and dynamics. This, was coupled with the development of simulation methods to calculate spectra from quantum time correlation functions of extended system, by explicitly treating hundreds of degrees of freedom, without making any assumptions of separability. Significant progress has also been made in mass spectrometric analysis of doped clusters, the complete understanding of which requires detailed descriptions of ionization, and hole migration dynamics. These developments still continue. With the applied ends in mind, we had identified the quantitative characterization of energy content of HEDM materials as crucial, and as such developed and implemented extremely sensitive calorimetry for characterizing O doped solid oxygen. This technology is available for transition.

5. The issue of stabilization by pressure, was only addressed in the studies of solid hydrogens coated with Xe overlayers. These studies confirm the concept.

With respect to scale-up, two aspects are to be understood: scaling up the dopant density, and the preparation of gram size samples. Both of these goals were met in the case of O/O₂ samples, where number densities are conservatively estimated at ~1% and milligram size samples were prepared. In part, due to the lack of outside interest, we did not pursue efforts to further scale-up the systems under study.

6. The rheology of hydrogen films was investigated in some detail. This was regarded as a study of fundamental importance in applications. Given the preparation of a hydrogen based fuel, its delivery will involve surfaces, therefore the rheology of the sample at such surfaces is crucial to understand. It was discovered that solid hydrogens have peculiar transport properties on surfaces.

7. We never reached the stage of field tests, even though, the O/ O₂ system deserved this consideration.

III. HIGHLIGHTS OF ACCOMPLISHED RESEARCH (1996-1997)

There have been annual reports, annual presentations at the HEDM contractors meeting, followed by extended abstracts of the presentations made at these meetings, and a significant number of publications that have resulted from research through the URI. The content of those reports will not be reiterated here, rather, we will emphasize the developments over the last year.

1. Photodynamics in cryogenic solids, Solid Hydrogens and Helium (V. A. Apkarian):

The original target of our studies was the preparation and characterization of advanced cryogenic propellants, in the form of doped solids, and in particular solid hydrogens. A fundamental understanding of these systems on first principles basis, and at the atomic level of detail, constitutes a subset of the grand challenge to chemical physics today, namely, an understanding of many-body interactions and dynamics. This now seems the target also embraced by the AF HEDM program, and our researches are almost entirely dedicated to this general area: understanding many-body interactions and electronic landscapes beyond the Born-Oppenheimer separation, through experiment and theory. During the last year we have made some highly significant advances in this general area, much of it outlined in the appended publication list. I will present some of the highlights of our achievements in the context of the more general field.

A) Ultrafast spectroscopy / classical molecular dynamics, to See and to Control atomic motions in condensed media in real-time: The experiments in this case involve preparation of superposition states in a time short compared to any dynamical recursions in the system, under which condition, it can rigorously be shown that the evolving dynamics and its observables are accurately described by the classical Hamiltonian, and by assuming the classical Franck principle for describing the matter-radiation interaction. We have demonstrated that even in dissipative media, vibronic coherences can be prepared, and will retain memory of the coherence of the laser pulse that prepares them, for time scales of ~ 10 ps, long enough to effect control over chemistry [5,6]. Moreover, we have proceeded beyond the one-dimensional inversion of trajectory data, to analyze the multidimensional information content, and in particular to extract from the experiments and simulations the dynamical solvation of electronic states and the lattice motions accompanying a chromophore excitation [14]. Solvent induced non-adiabatic dynamics is one of the more important perturbations that arises in condensed media, one that can change the course of chemistry. As such, we have carried out one of the most detailed measurements of this process in both solid and liquid phase, and demonstrated that solvent symmetry can play a crucial role in inducing transitions [10,11]. This work has shown that one of the most common mechanisms for solvent induced non-adiabaticity is dipolar coupling between electronic states, a coupling that is completely canceled in sites of cubic or

higher symmetry. Thus, where predissociation may occur within a single vibrational period in the liquid phase, may be completely absent in the solid phase [10].

B) Frequency domain observables - Quantum many-body time correlations: in contrast with the ultrafast time domain studies where population densities are created and interrogated, long time observables, or frequency domain spectroscopy, are related to quantum amplitudes and their time correlations. Exact methods for time propagation of quantum Hamiltonians of systems of large dimensionality do not exist. All existing methods involve abstractions, or approximations such as separability, that are difficult to ascertain. We have recently devised the method of mixed-order semiclassical molecular dynamics, in coordinate representation [3,9], and more recently in coherent state representation [13], that is essentially exact for the short times relevant for frequency domain spectroscopy in condensed media. The method, has been applied to linear and nonlinear spectroscopy, to the analysis of absorption, emission, and resonant Raman spectra in solids. Particularly impressive is the most recent application, in which zero-phonon lines and phonon sidebands that depend on the level of vibrational excitation of a chromophore, have been reproduced by explicitly simulating the quantum amplitudes of a system of 320 degrees of freedom [13]. No other method could accomplish this.

C) Many-body potentials: we have learned how to propagate quantum and classical Hamiltonians for systems of large dimensionality. For the complete characterization of condensed phase Hamiltonians, and to dissect experimental observables at the atomistic level of detail, it is necessary to devise efficient and accurate approaches to the description of interactions i.e. the construction of many-body potentials. We have, for sometime, been investigating methods for relating pair interactions to many-body interactions while quantitatively accounting for non-additivities. We now have such a method, namely the diatomics-in-molecules formalism, where charge transfer states are explicitly included, and where the ionic state energies are computed by vector summations [8,12]. The method was developed by considering dimers for which detailed information regarding potentials, and their non additivities existed. The most impressive of these demonstrations is the most recent, namely the HF-dimer, which represents the best studied prototype of hydrogen bonding. We have been able to reproduce the global surface for this system, with an accuracy of ~1% for all energies and coordinates, with pair parameters as the sole input [12]. This is a fundamental development, that may be expected to have a major impact on future atomistic treatments of condensed phase systems.

D) Dynamics in Quantum Hosts: We have developed a rather approximate, nevertheless useful method of dynamical simulations in quantum hosts such as hydrogen and helium, in the form of classical simulations over pseudo-potentials constructed variationally [5,7]. This has enabled us to carry out

dynamical simulations to reproduce structure, reactivity, and local dynamics of impurities isolated in solid hydrogen. The simulations agree, and rationalize our experimental observations. The exception remains the absence of reaction in the case of $O(^1D)$ isolated in solid hydrogen. We believe this failure is the result of the inaccurate treatment of potentials, an issue that we continue to explore.

E) O and O_2 doped solid Hydrogens: Rather extensive reports on this subject have been given at prior HEDM meetings and in several earlier manuscripts. During the last year, a report [17], and two manuscripts appeared on the subject [5,7]. A final manuscript, including experiments on O, XeO, $O_2:O$, in solid hydrogens remains in preparation [16]. These studies have demonstrated the feasibility of preparation of O doped solid hydrogens, and their stability. Some of the main conclusions of the work are: a) experimentally we find that atomic oxygen, $O(^3P, ^1D, \text{ and } ^1S)$, is not reactive with D_2/H_2 at cryogenic temperatures, theory still predicts that $O(^1D)$ is reactive. We believe this to be a shortcoming of the theory rather than the experiment, nevertheless this remains a challenge to understand. b) Theory shows that the lattice locally distorts around impurities developing a cage that fits the impurity like a glove, arresting molecular rotations, and stabilizing atomic dopants. These findings rationalize the experimental observations that laser induced fluorescence from molecular oxygen is polarized (no rotation) and that atomically doped solids are stable up to 9 K, when self-diffusion and melting of the host leads to macroscopic changes in the morphology of the solid with concomitant loss of all dopants. d) theory and experiment concur that solid H_2 when doped has a more stable lattice, and a higher density than when not doped, and the theoretical activation energy for diffusion and recombination is of order 120 K. All of the above indicate that macro samples of highly doped O/H_2 should be possible to engineer. At present, we have directed our attention to the preparation of macroscopic samples of O doped O_2 , based on findings of their stability and energy content through calorimetry (see below).

1. Hill, M. W.; and Apkarian, V. A.; *J. Chem. Phys.*, 105, 4023 (1996).
"Photodynamics of Charge transfer and Ion-Pair States of Xe:Cl₂ complexes in Liquid Ar"
2. Callicoatt, B.; Mar, D. D.; Apkarian, V. A.; Janda, K. C.; *J. Chem. Phys.* 105, 7872 (1996). "Charge Transfer Within He Clusters"
3. Ovchinnikov, M. and Apkarian, V. A., *J. Chem. Phys.*, 105, 10312 (1996).
"Condensed Phase Spectroscopy from mixed order semiclassical molecular dynamics: absorption emission and resonant Raman spectra of I₂ isolated in solid Kr"
4. Apkarian, V. A. *J. Chem. Phys.* 106, 5298 (1997).
"On time resolved Laser Induced Harpoon Reactions."
5. Li, Z.; Apkarian, V. A.; Harding, L. B. *J. Chem. Phys.* 106, 942 (1997).
" A theoretical investigation of solid hydrogens doped with atomic oxygen"
6. Bardeen, C. J.; Che, J.; Wilson, K. R.; Yakovlev, V. V.; Apkarian, V. A.; Martens, C. C.; Zadoyan, R.; Kohler, B.; Messina, M.; *J. Chem. Phys.* 106, 8486 (1997).
"Quantum Control of I₂ in the gas phase and in Condensed phase Solid Kr Matrix"
7. Li, Z; and Apkarian, V. A.; *J. Chem. Phys.* 107, 1544 (1997).
"Impurity Rotations in Quantum versus Classical Solids: O₂ in solid hydrogens"
8. Grigorenko, B. L.; Nemukhin, A. V.; and Apkarian, V. A.; *Chem. Phys.* 219, 161 (1997).
"Inclusion of ion-pair states in the Diatomics-In-Molecules description of potential energy surfaces: van der Waals complexes: He-Cl₂ and Ar-Cl₂"
9. Ovchinnikov, M. and Apkarian, V. A., *J. Chem. Phys.*, 106, 5775 (1997).
"Quantum Interference in Resonant Raman Spectra of I₂ in Condensed Media"
10. Zadoyan, R.; Sterling, M.; Ovchinnikov, M.; and Apkarian, V. A. *J. Chem. Phys.* (in press, 1997).
"Predissociation dynamics of I₂(B) in liquid CCl₄ observed through femtosecond pump-probe measurements: Electronic Caging through solvent symmetry"
11. Benderskii, A. V.; Zadoyan, R., Apkarian, V. A., *J. Chem Phys.* (in press, 1997)
"Caged Spin-Orbit Excited I*(²P_{1/2})+I*(²P_{1/2}) Atom Pairs in Liquids and in

Cryogenic Matrices: Spectroscopy and Dipolar Quenching"

12. Grigorenko, B. L.; Nemukhin, A. V.; and Apkarian, V. A., *J. Chem. Phys.* (submitted)
"Hydrogen bonding within the diatomics-in-molecules treatment: the HF dimer"
13. Ovchinnikov, M.; and Apkarian, V. A., *J. Chem. Phys.* (submitted)
"Mixed-Order Semiclassical Dynamics in Coherent State Representation: The connection between Phonon Sidebands and Guest - Host Dynamics"
14. Zadoyan, R.; Almy, J.; and Apkarian, V. A.; *J. Chem. Soc. Far. Disc.*, (submitted).
"Lattice Dynamics from the "Eyes" of the Chromophore: Real-Time Studies of I₂ Isolated in Rare Gas Matrices"

Manuscripts in Preparation:

15. Apkarian, V. A. and Schwentner, N.
a review article on "Molecular Photodynamics van der Waals Solids"
16. Danilychev, A. V., Kajihara, H., Tanaka, S., Koda, S., Apkarian, V. A.;
"Atomic Oxygen in Solid Hydrogen"

Published Proceedings (Sept. 1996 -Sept. 1997)

V. A. Apkarian

17. V. A. Apkarian, Proceedings of HEDM Conference (Washington DC, 1997)
"Spectroscopy and dynamics in Quantum vs. Classical Solids"

INVITED TALKS (Sept. 1996 - Sept. 1997)

V. A. Apkarian

10/96 UC Berkeley

11/96 University of Utah (Salt Lake City, Utah)

12/96 California Institute of Technology (Pasadena, CA)

3/97 National Meeting of American Physical Society (Kansas City)

4/97 Lineberger Symposium (USC, LA, CA)

4/97 Free University of Berlin (Berlin, Germany)

5/97 Lineberger Symposium (USC, LA, CA)

- 5/97 Max Planck Institut für Strömungsforchung, (Göttingen, Germany)
- 5/97 Tri-University Seminar (Berlin, Germany)
- 5/97 University of Lausanne (Lausanne, Switzerland)
- 5/97 Max Born Institute (Aldershoff, Germany)
- 6/97 HEDM Contractors Meeting (Washington DC)
- 6/97 University of Koeln (Koeln, Germany)
- 6/97 Chemical Society Colloquium, Technical University (Munich, Germany)
- 6/97 Conference on Quatum Clusters (Schloss Ringberg, Tegernsee, Germany)
- 6/97 Theoretical and Physical Chemistry, FUB (Berlin, Germany)
- 8/97 Int. Conf. on Chemistry and Physics in Matrices (Spital am Pyhrn, Austria)
- 9/97 Am. Chem. Soc. National Meeting (Las Vegas, Nevada)
- 9/97 Chem. Phys. Institute, Univ. of Oregon, Annual Retreat(Charleston, Oregon)

2. Mass Spectrometry of Doped He Clusters: Toward a Pick-up Synthesis of HEDM Materials (K. C. Janda):

Our group has been investigating the usefulness of liquid helium clusters as a medium for the synthesis of high energy density materials. Liquid helium clusters have exciting prospects in this regard since they offer a unique low temperature, high thermal conductivity environment for stabilizing reactive species. However, one difficulty with working with these clusters is that it is difficult to analyze their content. In this regard, we have been investigating the ionization and fragmentation of liquid helium clusters with and without dopant molecules. In particular, we have been investigating the mass spectra that are observed when clusters that contain between 500 and 10,000 atoms are ionized by 65 volt electrons.

Even the mass spectrum of pure helium clusters has proved to be quite surprising. Of course, one expects significant fragmentation when such clusters are ionized, since it takes only about 0.001 eV to evaporate a helium atom from a large cluster. Even so, the extent of fragmentation is surprising. An example of a mass spectrum is shown in Figure 1. Although the cluster starts out with 1100 atoms, the most intense peak after fragmentation is He_2^+ . For 10,000 atom clusters, the most prominent ion in the mass spectrum is still He_2^+ . Why is this surprising? Consider the fact that the energy of formation of He_2^+ is 2.5 eV. Even if all of this energy went into the evaporation of He atoms, and as little energy as possible were consumed in the evaporation of each atom, this would only account for the evaporation of about 3,000 atoms. For He_2^+ to be observed upon ionization of a 10,000 atom cluster, evaporation can not be the main fragmentation mechanism. We conclude that the dynamics of cluster ionization must be considerably more complicated than we had expected. Although He_2^+ is the most common product ion that is observed, He_n^+ ions with n up to 90 appear in the mass spectrum. There are "magic numbers" for n = 10 and 14. The last of these magic numbers corresponds to a He_2^+ core surrounded by a first shell of 12 helium atoms. It is not obvious that such shell structure should occur for a quantum liquid. The magic number at 10 indicates that the small ionized clusters can not be described by a simple combination of two body forces between the shell atoms and the He_2^+ or a He_3^+ core.

Pure Helium Cluster Mass Spectrum

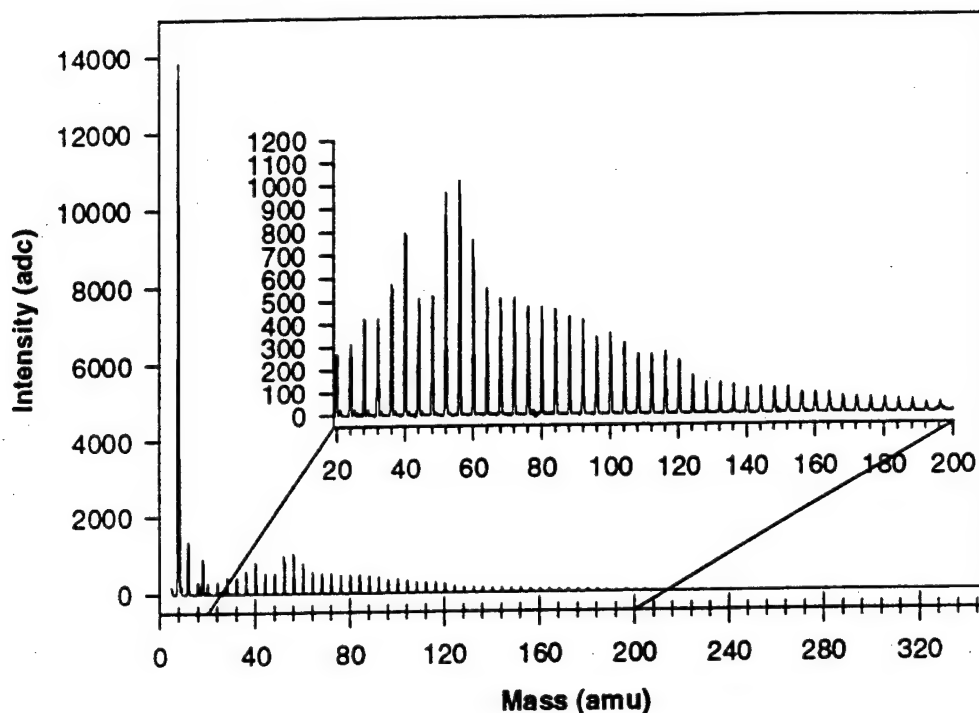


Fig. 1 This figure shows a mass spectrum that results when a 1100 atom He cluster is ionized with 65 eV electrons. About half the total intensity is in the He_2^+ , and He_3^+ is the next most intense peak. The peaks for He_{10}^+ and He_{14}^+ are also more intense than the adjacent peaks. This indicates that there are specific chemical interactions that determine the stability for ionic He clusters in this size range. The mass spectrum continues to about He_{90}^+ before the signal completely disappears into the base line. To our surprise, this pattern of fragmentation results even for ionization of much larger clusters. This indicates that the energy dissipated by the "charge localization" is not dissipated simply as heat.

We have also made extensive studies of liquid helium clusters that contain Ar and NO dopant species. Among our observations are the following phenomena. When a cluster containing 1100 helium atoms and a single Ar atom is ionized, the chance that the Ar atom ends up being ionized is about 20%, and this chance drops very quickly with increasing numbers of helium atoms. The Ar^+ ion tends to be formed with a shell of helium atoms around it. When a cluster that contains 1100 helium atoms and two Ar atoms is ionized, the chance that Ar_2^+ is formed is 30%, and no helium atoms tend to stick to the Ar_2^+ species. Finally, when a cluster that contains 1100 helium atoms and 3 Ar atoms is ionized, the chance that Ar_3^+ is formed is close to zero! The liquid helium cluster is surprisingly inefficient at

"caging" this species. An example of data from which these types of conclusion are drawn is shown in Figure 2. In contrast, ionization of helium clusters that contain NO is much more likely to result in the observation of NO^+ than N^+ in spite of the fact that the NO^+ is created 2.5 eV above its dissociation limit. In this case, the helium clusters are very efficient at "caging" a high energy species. We will present preliminary models that help us explain some, but not all, of these phenomena.

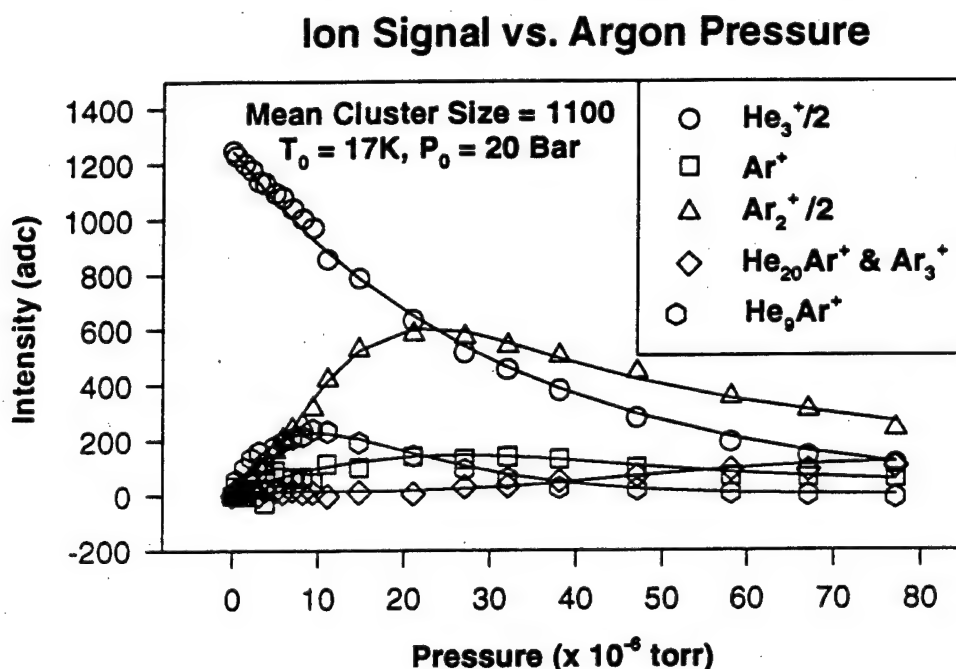


Fig. 2. This figure shows several ion signal intensities as a function of the Ar pressure in the pick up cell. The lines through the data points result from statistical modeling of the data. The fit to the data shows, for instance, that if the cluster contains a single Ar atom, then the probability that the charge ends up on that atom is 20%.

We believe that we have made important progress in understanding how to use He clusters to prepare the type of species that are important to the HEDM program. However, the analysis of the system may not be straight forward. For example, Figure 3 shows both a raw mass spectrum of a 1100 atom He cluster that has passed through a pick-up cell containing 3.1×10^{-6} torr of Ar. The raw data shows no obvious indication that the cluster has picked up an Ar atom. However, when the mass spectrum of a pure helium cluster beam is subtracted from that

shown in Figure 3, the difference spectrum in Figure 4 results. This difference spectrum mainly consists of mass peaks of the type Ar^+He_n with $1 < n < 13$. We would expect similar phenomena to occur if boron atoms were being picked up. The mass spectrometry will have to be worked out on a case by case basis.

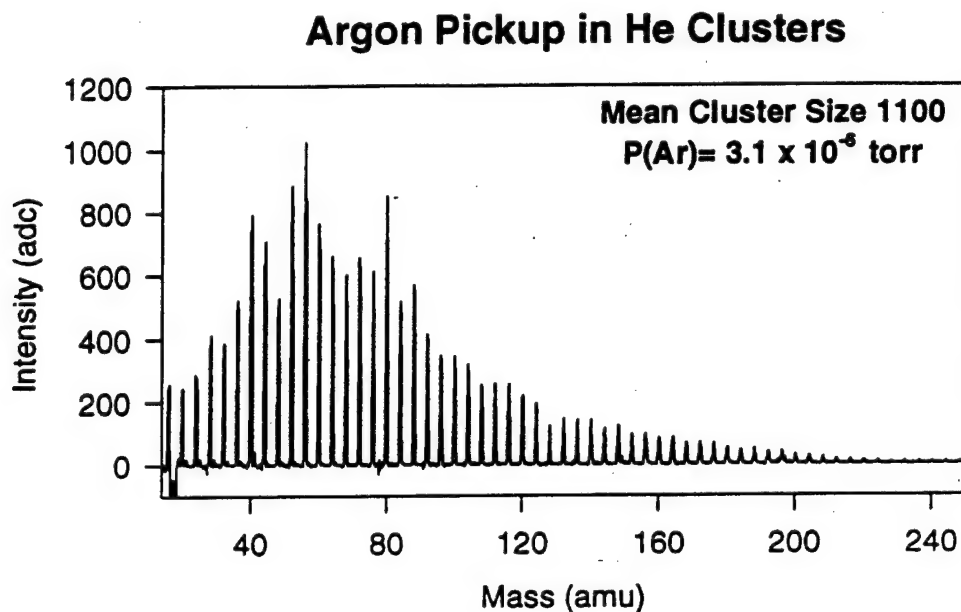


Figure 3. This figure shows a portion of the mass spectrum that results if an 1100 helium atom cluster passed through a pick-up cell containing 3.1×10^{-6} torr of argon. The spectrum is almost unchanged from that of Figure 1. It is not obvious that any argon has been picked up by the cluster.

Argon Pickup in He Clusters Pure He Subtracted

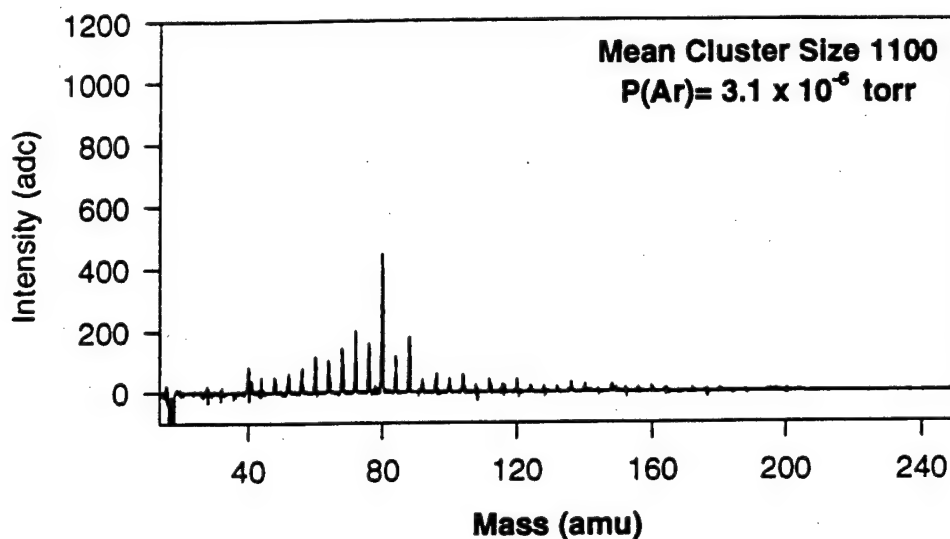


Figure 4. This figure shows a difference spectrum in which data from Figure 1 is subtracted from that in Figure 3. The difference spectrum shows that Ar has been picked up, and that the resulting mass peaks are mostly of the type Ar^+He_n with $1 < n < 13$.

We believe that the data we have obtained to date would allow us to design the cluster synthesis part of an apparatus to form boron/hydrogen HEDM materials. We recommend that work proceed to determine whether the condensation part of the technique is feasible.

1. High resolution spectroscopy of the $\text{He}^{79}\text{Br}_2$ van der Waals molecule: An experimental and theoretical study, Douglas G. Jahn, William S. Barney, Jerry Cabalo, Simon G. Clement, Timothy J. Slotterback, Jason Williams, Kenneth C. Janda and Nadine Halberstadt, *J. Chem. Phys.* **104**, 3501 (1996).
2. Charge transfer within He clusters, Berton Callicoatt, David D. Mar, V.A. Apkarian and Kenneth C. Janda, *J. Chem. Phys.* **105**, 7872 (1996).
3. Differential scattering cross sections for HeCl_2 , NeCl_2 , and ArCl_2 : multiproperty fits of the potential energy surfaces, Andreas Rohrbacher and Kenneth C. Janda, Laura Beneventi, Piergiorgio Casavecchia and Gian Gualberto Volpi, *J. Phys. Chem.* **101**, 6528 (1997, Y.T. Lee Issue).
4. The Resonant Charge Hopping Rate in Positively Charged Helium Clusters, N. Halberstadt and K.C. Janda, *Chem. Phys. Letts.*, submitted (1997).

Manuscripts in Preparation:

5. Magic Numbers in Ionized Liquid Helium Droplets: A New Interpretation, B. E. Callicoat, K. Forde and K. C. Janda
6. Charge Transfer Probability from He^+ ions to Ar atoms In Liquid Helium Droplets, B. E. Callicoat, K. Forde, T. Ruchti and K. C. Janda

Invited Talks:

K. C. Janda

1. The Structure and Dynamics of Small van der Waals Clusters, Department of Physics, Arizona State University, September 14, 1995.
2. Measuring the wave functions of small molecules and clusters, Harvard-MIT joint seminar, October 19, 1995.
3. Two Different Ways to Measure the Wave Function of a Halogen Molecule, Department of Chemistry, Hebrew University, January 15, 1996.
4. Two Different Ways to Measure the Wave Function of a Halogen Molecule, Department of Physical Chemistry, Weizmann Institute, January 17, 1996.
5. Two Different Ways to Measure the Wave Function of a Halogen Molecule, Department of Physical Chemistry, University of Tel-Aviv, January 18, 1996.

6. Rare Gas Halogen Potentials: They are more complicated than we thought! Symposium on Atomic, Surface and Cluster Physics, Engleberg, Switzerland, January 26, 1996.
7. The Kinetics of H₂ Desorption from Si and Ge Surfaces, Analytical Services Group, Ceiba-Geigy Corporation, Basel, Switzerland, March 8, 1996.
8. Two Different Ways to Measure the Wave Function of a Halogen Molecule, Laboratoire Collisions, Agregats, Reactivite, Universite Paul Sabatier, Toulouse, France, March 15, 1996.
9. Characterization of Liquid Helium Clusters by Mass Spectrometry, HEDM Contractors Meeting, AFOSR, June 6, 1996
10. Measuring how molecular wavefunctions change with bond length, Chemistry Department Seminar, California State University, Fullerton, California, September 5, 1996
11. Mass Spectrometry of Doped Helium Clusters, Institute of Mathematics and Fundamental Physics, (C.S.I.C.) Madrid, Spain, October 30, 1996.
12. Charge Transfer in Liquid Helium Clusters, Joint Seminar, Molecular Physics, University of Lausanne and Chemical Physics, Ecole Polytechnique Federale de Lausanne, Lausanne Switzerland, 11 November, 1996
13. Charge Transfer in Liquid Helium Clusters, Laboratoire Collisions, Agregats, Reactivite, Universite Paul Sabatier, Toulouse, France, November 22, 1996.
14. Charge Transfer in Liquid Helium Clusters, Laboratoire de Photophysique Moleculaire, Universite de Paris-Sud, Orsay, France, December 6, 1996.
15. Charge Transfer in Liquid Helium Clusters, American Physical Society Meeting, Kansas City Missouri, March 19, 1997.
16. Charge Transfer in Liquid Helium Clusters, Department of Chemistry, Iowa State University, March 21, 1997.
17. Mass Spectrometry of Doped Liquid Helium Clusters, HEDM Contractors Meeting, AFOSR, June 2, 1997

3. Preparation and characterization (P. Taborek and J. Rutledge):

1. Rheology in solid hydrogens: We have completed our studies of the surface mass transport of solid hydrogen species. Both frozen H₂ and D₂ exhibit high rates of surface transport which is thermally activated even at temperatures below 2K. The activation energy for surface transport is much lower than for bulk diffusion, so surface recombination will be the dominant loss mechanism for atomically doped hydrogen. Our results have been published in K.G. Sukatme, J.E. Rutledge, and P. Taborek, J. Low Temp Phys. 103, 301 (1996)

2. Calorimetry and Source development for solids doped with atomic oxygen: Although a number of techniques for making atomically doped cryogenic solids have been proposed and tested, there have been no reliable measurements of the absolute atom concentration or the energy content of the metastable solids. Calorimetry is a technique which directly measures the energy released when atoms recombine, so it is a particularly useful method for assessing the quality of cryogenic HEDM materials. We have built an apparatus which consists of a plasma atom source and appropriate plumbing to conduct the atoms to a low temperature calorimeter. Our experiments have concentrated on isolating atomic oxygen formed in the plasma in either argon or molecular oxygen. The apparatus is also equipped with an optical fiber to monitor thermoluminescence, but surprisingly, optical emission has proved to be only weakly correlated with the energy content of the samples.

There are two conflicting thermal requirements for the calorimeter. While the sample is being deposited, considerable amounts of heat must be removed, so during deposition the sample should be in good thermal contact with the refrigerator. On the other hand, the energy content of the sample is measured by thermally isolating it and detecting an increase in the temperature. We have satisfied these requirements by building a mechanical heat switch which can reduce the coupling of the calorimeter to the refrigerator by several orders of magnitude in a fraction of a second. We have built two versions of the calorimeter. In our first experiments, we were particularly concerned about heat transfer due to evaporation or sublimation of the solid sample, so the calorimeter cell was connected to the plasma source with vacuum tight plumbing. Our subsequent experience with this design convinced us that the interesting energy release occurred at temperatures so low that sublimation was not important. We have therefore simplified the plumbing and increased the sensitivity of the calorimeter by using an open geometry in which the gas from the plasma source is condensed onto a plate attached to the heat switch. Even when the heat switch is closed and the calorimeter is thermally anchored to the refrigerator, a few milliwatts of absorbed power results in a readily detectable temperature rise. We have used this fact to monitor the deposition of the samples. Unactivated diatomic gas produces a thermal signal which corresponds to the latent heat of fusion of the sample. Gas which has passed through the plasma typically gives a larger temperature rise during deposition, due to recombination of atoms at the growth surface. This thermal recombination

signal provides a quantitative measure of the combined efficiency of the plasma atom source and the atom transport plumbing. The source efficiency is determined by the equilibrium atom concentration in the plasma and the recombination rate on the walls of the tubing used to transport the atoms to the calorimeter.

Optimising the efficiency of the atom source has been an important goal of this work. We have evaluated a number of different source types including microwave, DC and RF, and have studied the dependence of the wall recombination rate on length, radius and wall coating and flow rate. The source efficiency is sensitively dependent on several factors. Our initial sources produced beams which were approximately 2% atoms, but these were improved until we achieved beams of essentially 100% atoms. The final source configuration is based on a helical coil RF source operating at 14MHz. The gas pressure is 0.3 Torr, and the flow rate is 0.3 sccm. The transport system uses 1 inch quartz tubing. The plasma is injected into the vacuum system through a boron nitride nozzle which produces a supersonic atom beam. Details of the source have been described in a patent disclosure which has been analyzed by a law firm specializing in aerospace patents. They have advised the University that, in their opinion, the invention is patentable.

Another crucial feature of our deposition technique is to maintain the growth surface below approximately 8K. It is important to note that even a small heat flux from, for example, the latent heat of fusion of the sample, can raise the temperature of the growth surface above this value even if the substrate is nominally much colder. The surprisingly low value of the thermal conductivity of cryogenic solids places a stringent upper limit on the surface heat flux. Our previous studies have shown that surface molecules of cryogenic solids are quite mobile even at temperatures 1/5 of the triple temperature. Samples with the highest energy content were always grown at the lowest temperatures (~6K). Samples grown at 15K have no detectable heat release due to recombination of atoms, because the surface mobility is so high that recombination takes place during growth.

After the sample is deposited, it is thermally isolated by opening the heat switch and the temperature is allowed to rise. The residual heat leak into the sample is due to the black body radiation from the 25K heat shield. Both the heat leak and the background heat capacity of the empty calorimeter have been accurately determined. Applying the conservation of energy yields the heat liberated by the sample. A background source of heat can be detected even in samples made of pure diatomic gas; this is due to hysteresis in the alpha to beta phase transition in solid oxygen, which has a small latent heat. In our earliest samples, the heat due to atom recombination was similar in magnitude to this latent heat background, and it was difficult to distinguish the two effects. This was also a source of error in similar studies in the 60's. With our optimized source configuration, however, the heat released due to recombination is an order of magnitude larger than the background. The amount of heat released can be converted into an estimate of the atom concentration since the heat of formation of O is well known. The main uncertainty in our estimate is the

sticking coefficient of the atom beam. This is complicated by the fact that most of the beam recombines in highly exothermic reactions on the surface, and these hot reaction products are unlikely to stick. A measurement of the heat capacity of the sample provides a crude estimate of the sticking coefficient of <0.5 . The most conservative estimates of the O concentration based on a sticking coefficient of unity, is 0.5%, while a more realistic estimate yields concentrations greater than 1%.

In conclusion, the primary goal of our work on this project has been to establish the physical limits of atom concentrations in cryogenic solids formed from quenched plasma discharges. We have made substantial progress toward this goal. Our work has shown that the atom yield in the solid condensed samples depends very sensitively on a large number of process parameters. We have made dramatic improvements in both the control of these process parameters and in the precision of our diagnostic calorimetry. These improvements have lead to the development of a protocol for making solid oxygen doped with approximately 1% atomic O. This represents an important milestone in HEDM research. Furthermore, the process does not rely on exotic technology, is relatively cheap, and is scalable to larger samples. The most important scientific and engineering issues which should be pursued to further improve this technology are the spectroscopic monitoring of the recombination in the solid, refining measurements of the sticking coefficient, and improving the refrigeration so that the solid can be grown at higher rates and at lower temperatures.

Publications

P. Taborek, J. Rutledge

1. DeVecchio, P. Taborek, and J.E. Rutledge, Rev.Sci. Inst. 66, 5367 (1995).
2. Sukatme, J.E. Rutledge, and P. Taborek, J. Low Temp Phys. 103, 301 (1996).
3. E. Rutledge and P. Taborek , J. Appl. Phys. Lett. (submitted).

4. Theory (R. B. Gerber)

REPORT ON RESEARCH SUPPORTED BY THE IRVINE UNIVERSITY RESEARCH INITIATIVE OF AFOSR

The research of our theoretical group in the framework of this project focused on: (1) Development of simulation methods for cryogenic materials (2) Applications of these methods to obtain data on systems of interest as potential cryogenic propellants. The properties we computed included: Microscopic, atomic-scale structure of cryogenic materials (e.g. hydrogen clusters doped by energetic species); Energetic stability of cryogenic systems, such as doped hydrogen clusters; Dynamical processes following electronic excitation of atoms and of diatomic molecules in cryogenic media; Nonradiative decay of excited electronic states of atoms and molecules in cryogenic materials; Separation and recombination of fragments following photodissociation of molecules in cryogenic solids or clusters. The methods developed, and the data obtained in the various simulations are described in a series of articles acknowledging URI support, which are listed later. Some of the articles describe work supported by URI/AFOSR, while others acknowledge partial support by URI with additional support from another source. We give below a very brief outline of the main results.

(1) Electronic energy decay and orbital reorientation of excited atom states in cryogenic matrices:

Time-scales were computed for electronic energy decay of excited $F(2P)$ atoms in rare-gas solids, and for the p-orbital reorientation (related to polarization change) in this system. These calculations were done for relatively heavy rare-gas atoms (Ar, Kr), and using semiclassical methods, but the data on the timescales of the electronic transitions should be useful also for anticipating behavior in quantum solids. The lifetimes of excited electronic states are important for characterizing the interactions of doping species with the cryogenic environment. This work is described in articles Nos. (1) and (3) in the list of URI supported publications.

(2) Photodissociation and recombination of molecules in a cryogenic solid:

The photodissociation of diatomic molecules in a cryogenic matrix, including the events of electronic energy relaxation and of recombination of photofragments, was studied by semiclassical Molecular Dynamics Simulations, that include (nonadiabatic) transitions between electronic states. Calculations on HCl in Ar (No. 9 in list of supported publications) provided quantitative data on the photoproduct separation/recombination ratio, and on the factors that determine it, and also on the time-distributions of these types of events. Transitions between different electronic states in this system were found to be very frequent and efficient.

(3) Method for time-dependent quantum simulations of many atom systems:

Our research on this topic was mostly supported by a Phillips Laboratory Contract and by the Chemistry Division of NSF. However, important results were obtained also in the URI project. The development began as a simple but useful approximation for quantum simulations of large systems, assuming separability of different collective degrees of freedom (Classical Separable Potential method - Nos. 4 and 5 on lists of supported publication). The method was extended into a fairly rigorous algorithm for time-dependent quantum simulations, including effects of correlation's between modes yet practically applicable to much larger systems than has hitherto been possible. Among the contributions in the framework of the URI was a study showing this type of method can be very successful for hydrogen clusters (no. 7 on the list of publications).

(4) Survival of quantum clusters in collisions:

We used quantum dynamics calculations to show that there are surprisingly large probabilities for weakly bound hydrogen and doped hydrogen clusters to survive collisions with atoms. (No. 2 in list of publications). This surprising dynamical stability can be used in strategies for making doped hydrogen propellants.

(5) Structure and stability of $\text{Mg}(\text{H}_2)_n$ clusters:

Diffusion Quantum Monte Carlo simulations have shown that in large $\text{Mg}(\text{H}_2)_n$ clusters, $n \geq 12$, the Mg atom is "buried" inside the H_2 envelope (No. 8 on list of supported publications). Feynman path integral simulations were used by us to show that this behavior is maintained up to the evaporation temperature of the cluster. The computations show that isolated Mg atoms in solid hydrogen should remain stable against diffusion until at least 4K, which is encouraging for the use of magnesium-doped solid hydrogen as a cryogenic propellant.

The main results of our theoretical and computational studies during the third year of the URI project on Advanced Cryogenic Materials were on the following three subjects: (1) Characterization of the solvation properties of magnesium atoms in large hydrogen clusters, and in solid hydrogen. In particular, the dependence on temperature of the stability and structure of the metal-hydrogen clusters was determined. (2) A user-friendly code for quantum mechanical simulations of the time-evolution of photochemical and photophysical processes in large systems was developed. The code will be made available to the community very shortly, and provides a convenient tool for simulations of spectroscopy and dynamics in many systems exhibiting large quantum effects (as is the case for cryogenic propellants). (3) The dynamics following electronic excitation of $\text{Li}(\text{Ne})_{17}$ clusters was studied by quantum simulations, and the vibrational properties of this cluster in its electronic ground state were determined. Interesting results were obtained regarding the structure of this system, and the use of electronic spectroscopy to characterize it.

- (1) A.I. Krylov, R.B. Gerber and V.A. Apkarian
Adiabatic Approximation and Non-Adiabatic Effects for Open-Shell Atoms
in Inert Solvents: F Atoms on Solid Kr
Chem. Phys. **189**, 261-272 (1994). (Special issue on Processes in Solid
Matrices).
- (2) Z. Li and R.B. Gerber
Survival of Weakly Bound Quantum Clusters in Collisions with Atoms
Chem. Phys. Lett. **229**, 650-656(1994).
- (3) A.I. Krylov and R.B. Gerber
Reorientation Dynamics of Electronic Orbitals in Condensed Phases:
Simulations of F(²P) Atoms in Solid Kr
Chem. Phys. Lett. **231**, 395-400 (1994).
- (4) Z. Li and R.B. Gerber
Electronic Excitation Dynamics of Li(H₂)₂: Dissociation Mechanisms,
Lifetimes, and the Validity of a Hybrid Quantum/Classical Approach
J. Chem Phys. **102**, 4056-4062 (1995).
- (5) P. Jungwirth and R.B. Gerber
Quantum Dynamics of Large Polyatomic Systems Using a Classically-Based
Separable Potential Method
J. Chem. Phys. **102**, 6046-6056 (1995).
- (6) P. Jungwirth and R.B. Gerber
Quantum Dynamics of Many-Atom Systems by the Classically-Based
Separable Potential (CSP) method: Calculations for I⁺(Ar)₁₂ in Full
Dimensionality
J. Chem. Phys. **102**, 8855-8864 (1995).
- (7) Z. Li and R.B. Gerber
Validity of the Time-Dependent Self-Consistent Field (TDSCF)
Approximation for Non-Stationary Vibrational State of Quantum
Clusters
Chem. Phys. Lett. **104**, 5803-5814 (1995).
- (8) S. Broude and R.B. Gerber
Solvation of Metal Atoms in Quantum Clusters: Structural and Vibrational
Properties of Hg (H₂)₁₂, Mg (H₂)₁₂
Chem. Phys. Lett. **258**, 416-420 (1996).
- (9) A.I. Krylov and R.B. Gerber

Photodissociation Dynamics of HCl in Solid Ar: Cage Exit, Nonadiabatic Transitions and Recombination
J. Chem. Phys. **106**, 6754-6587 (1997).

Use of URI Support

R. B. Gerber

The URI support was used:

- (a) In partial support of postdoctoral co-workers and visitors (Dr. Z. Li, Dr. P. Jungwirth).
- (b) To support visiting graduate students working on the project when at UCI (S. Broude, A.I. Krylov).
- (c) To support Joon O. Jung, a UCI graduate student.

Invited Conference Lectures

R. B. Gerber

- (1) "Time-dependent quantum dynamics of clusters and solids", given at "Femtochemistry - the Lausanne Conference", in Lausanne, Switzerland, September 1995.
- (2) "Wavefunctions, spectroscopy and dynamics of proteins and of condensed phases", given at "Symposium on New Developments in Experimental and Computational Studies of Biomolecules", Beckmann Institute, Urbana, Illinois, November 1995.
- (3) "Dynamics of electronic and vibrational processes in weakly-bound clusters", given at "SASP - International Symposium on the physics of clusters and surfaces", Engelberg, Switzerland, January 1996.
- (4) "Quantum dynamics in low-temperature solids", given at "Symposium on Chemical Reaction Dynamics in Condensed Phases", Newport Beach, California, February 1996.
- (5) "Quantum Molecular Dynamics simulations of processes in large systems", given at "Symposium on time-dependent quantum mechanics", Freiburg, Germany, February 1996.
- (6) "Quantum Molecular Dynamics simulation of cryogenic clusters and solids", given at the "Symposium on Computational Chemistry, Geneva, Switzerland, April 1996.
- (7) "Wavefunctions, Spectroscopy and Dynamics of Large Clusters", given at the Gordon Research Conference on Clusters, Barga, Italy, May 1996.
- (8) "Wavefunction, Spectroscopy and Dynamics of Biomolecules and of Molecular

Aggregates," given at Czech-Israeli Symposium on Frontiers in Chemistry, Prague, April 1996.

- (9) "Quantum wavepacket simulations of large clusters", To be given at: TAMC (Conference on Theory of Atomic and Molecular Clusters), Lake Geneva, Wisconsin, September 1996.

II. PERSONNEL SUPPORTED:

In addition to the five active faculty members in this program, a large number of students and postdoctoral fellows are intimately involved in the project. Below is a list of the personnel who are at least in part involved in the URI projects, some are funded in part, by other sources. These are:

Avanesyan, S.	Postdoc (Visiting)	Chemistry
Barney, B.*	Ph.D. (expected 1997)	Chemistry
Benderskii, A.	Postdoc	Chemistry
Broude, S.*	Ph. D. Candidate (Visiting)	Chemistry
Calicoatt, B	Ph.D. (expected 1997)	Chemistry
Clement, S.	Postdoc	Chemistry
Danilvchev, A.	Ph.D. (1995)	Chemistry
Devecchio, D.	M.S. (1995)	Physics
Do, N.	Graduate Student	Physics
Fiedler, S.	Ph.D. Candidate (1st year)	Chemistry
Forde, K.	Ph.D. Candidate (3rd year)	Chemistry
Fredj, E.*	Ph. D. Candidate (Visiting)	Chemistry
Grigorenko, B.	Postdoc (Visiting)	Chemistry
Hay, T.*	Undergraduate	Chemistry
Hill, M.*	Ph.D. (1995)	Chemistry
Jahn, D.*	Ph.D. (1995)	Chemistry
Jamka, A.	M.S. Candidate	Chemistry
Jung, J.	Ph.D. Candidate (4th year)	Chemistry
Jung, L.*	Undergraduate	Chemistry
Jungwirth, P.	Postdoc (Visiting)	Chemistry
Kizer, K.	Ph.D. (1997)	Chemistry
Krylov, A.	Ph.D. (1995)	Chemistry
Li, Z.*	Postdoc	Chemistry
Maiken, E.	Ph.D. (1996)	Physics
Mancinelli, G.	M.S. (1994)	Physics
Mar, D.	Undergraduate	Chemistry
McCoy, A.	Postdoc (Visiting)	Chemistry
Ovchinnikov, M.	Postdoc	Chemistry
Perry, D.	Ph.D. Candidate (4th year)	Chemistry
Phillips, J.	Ph.D. Candidate (2nd year)	Physics
Rohbacher, A.	Postdoc	Chemistry
Rom, A.	Postdoc	Chemistry
Ross, D.	Postdoc	Physics
Segall, J.	Postdoc	Chemistry
Sterling, M.	M.S. (1997)	Chemistry
Su, D.	M.S. (1996)	Physics
Sukhatme, K.	Ph.D. (1997)	Physics
Tam, S.*	M.S. (1996)	Chemistry
Tanaka, S.	Graduate Student (Visiting)	Chemistry

Zadoyan, R.
Zhu, T.
Zoval, J.

Postdoc
M.S. (1996)
Ph.D. (1996)

Chemistry
Physics
Chemistry

** Indicates individuals who were involved in URI projects and did not receive any funding.*

III. INTERACTIONS

1. The URI hosted sabbatical visits by Prof. V. E. Bondybey, of the Technical University of Munich. He has started an effort, complementing work at Irvine, in condensed Hydrogen and Helium, in Munich. V. A. Apkarian visited the group in Germany in 1996, and will return for a more extensive collaboration in 1997.
2. The URI hosted a sabbatical visit by Prof. N. Schwentner, of the Free University of Berlin. He participated in experiments in He during his stay in Irvine, and plans to continue work in solid hydrogen which was initiated earlier, during V. A. Apkarian's three month stay in Berlin. The unique capabilities of this group, through access to synchrotron radiation, will enable studies that are not possible in Irvine.
3. The URI keeps in close contact with AF Phillips Laboratory at Edwards. Simon Tam, a member of the Phillips lab staff, after spending a year at Irvine, completed a Masters thesis titled, "Spectroscopy of Impurities Isolated in Solid He: Experimental", and received his degree in 1996. Extensive transfer of computational algorithms and consultation on simulations continues between Irvine and the Lab.

IV. DISCOVERIES

The scientific discoveries made during the past year, which are highly significant to the Air Force effort, have already been discussed under the heading of Accomplishments. Recognizing that O doped solid O₂ is a HEDM of utility to propulsion, and given the fact that a unique method for the preparation of such samples at the dopant levels that make it a candidate as propellant of enhance specific impulse, a patent application has been filed on "Method of producing High Energy Density Cryogenic Fuel", UC Case No. 97-295-1. This case has been positively reviewed by the patent lawyers, and is expected to be filed with the US Patent Office.

V. HONORS

V. A. Apkarian	Humboldt Award, 1996
K. C. Janda	Secretary Treasurer, <i>Division of Chemical Physics of APS</i> (reelected 1996-)
	Visiting Professor, <i>Univ. Paul Sabatier, Toulouse</i> (France)

R. B. Gerber

Editorial Board, *Chemical Physics* (1996-)

Editorial Board, *Berichte der Bunsengesellschaft für
Physikalische Chemie* (1994-)